Gaseous and Liquid Hydrogen

Los Alamos National Laboratory
Laboratory Implementation Guidance LIG 402-1200-03.0
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1.0 Introduction

1.1 Background

Several unique properties contribute to the hazards associated with gaseous and liquid hydrogen systems. First, hydrogen is flammable over a wide range of concentrations. Second, the ignition energy for hydrogen is very low. Third, a single volume of liquid expands to about 850 volumes of gas at standard temperature and pressure when vaporized; therefore, high gas pressure can be created when liquid hydrogen is vaporized in a confined system. Finally, some materials (including metals and, in particular, carbon steel) are embrittled by hydrogen and should never be used in hydrogen service.

Laboratory requirements for gaseous and liquid hydrogen systems are found in Laboratory Implementation Requirement (LIR) 402-1200-01, "Pressure, Vacuum, and Cryogenic Systems," LIR 402-580-01, "Cryogenic Fluids and Cryogens," and Laboratory Performance Requirement (LPR) 402-00-00.0, "Worker Health and Safety," Appendix 18, "Pressure/Cryogens." Upon the issue date of this Laboratory Implementation Guidance (LIG), Technical Bulletin 1403, "Gaseous and Liquid Hydrogen," is deleted.

1.2 In this Document

2.0 Purpose

The purpose of this LIG is to describe some characteristics of and hazards associated with hydrogen and to provide suggested considerations for safely designing, constructing, and operating hydrogen systems. The LIG also provides recommended emergency procedures for hydrogen leaks.

3.0 Scope

The information contained in this LIG should be reviewed and considered by all LANL workers involved in constructing and using gaseous and liquid hydrogen systems.

4.0 Definitions

4.1 Acronyms

atm	atmosphere
C&LGSC	Cryogenic and Liquefied Gas Safety Committee
CGPF	Compressed Gas Processing Facility
DOE	US Department of Energy
DOT	US Department of Transportation
ES&H	Environment, Safety, and Health
ESH-5	Industrial Hygiene and Safety (Group)
HCP	hazard control plan
kJ	kilojoule

LANL	Los Alamos National Laboratory
LA-UR	Los Alamos – Unrestricted Release
LIG	Laboratory implementation guidance
LIR	Laboratory implementation requirement
LPR	Laboratory performance requirement
μJ	microjoule
NFPA	National Fire Protection Association
psia	pounds per square inch (absolute)
psig	pounds per square inch (gauge)
vol %	percentage based on volume

4.2 Terms

C&LGSC—A Laboratory committee that provides a source of independent peer review at the Laboratory, providing advice and counsel to Laboratory groups and individuals on safe use of cryogenic and liquefied gases.

ES&H representative—Any individual with academic credentials, work experience, or extensive knowledge in an ES&H discipline (for example, industrial hygiene, industrial safety, health physics, or environmental protection) and in controlling the specific hazards associated with the defined work.

Explosion proof apparatus—Apparatus enclosed in a case that is capable of withstanding an explosion of a specified gas or vapor that may occur within it and of preventing the ignition of a specified gas or vapor surrounding the enclosure by sparks, flashes, or explosion of the gas or vapor within, and that operates at such an external temperature that a surrounding flammable atmosphere will not be ignited thereby.

Liquefied gas— An element or compound that can be maintained in the liquid state at room temperature by elevating the pressure.

National codes and national consensus standards—Documents published by nationally recognized organizations that reflect good engineering judgment and practices and that are regularly revised to incorporate changes in engineering, inspection, and fabrication practices.

Pressure relief system—A system designed to relieve excess internal pressure in any type of pressurized system. A pressure relief system includes pressure relief devices (i.e., safety valves, relief valves, and rupture disks) and piping or tubing to an approved release point.

Safety- and environment-responsible line manager—A manager or supervisor who is responsible for directing the day-to-day activities of employees under his/her supervision. See the definition in "Integrated Safety Management" (LA-UR-98-2837).

Worker—Any contract employee, subcontract employee, or visitor who performs work at the Laboratory.

5.0 Precautions and Limitations

This LIG provides guidance that, when considered for implementation, can help in meeting the requirements contained in LIR 402-1200-01, "Pressure, Vacuum, and Cryogenic Systems," and LIR 402-580-01, "Cryogenic Fluids and Cryogens," for gaseous and liquid hydrogen. However, it does not address all conceivable situations. You may contact the Industrial Hygiene and Safety Group or an ES&H representative for any special situations or additional guidance.

6.0 Guidance

6.1 Properties of Hydrogen

The properties and characteristics of hydrogen given in Table 1 are of special concern for safety.

TABLE 1

PHYSICAL PROPERTIES AND CHARACTERISTICS OF HYDROGEN
(Values Approximate)

Characteristic	Value
Color	None
Odor	None
Toxicity	Nontoxic
Density, liquid (boiling point)	4.4 lb/ft3 (0.07 g/cm3)
Boiling point (1 atm)	-423.2^{o}F (-252.9^{o}C)
Critical temperature (188.2 psia)	-400.4^{o}F (-240.2^{o}C)
Stoichiometric mixture in air	29 vol %
Flammability limits in air	4 to 75 vol %
Detonation limits in air	18 to 60 vol %
Minimum ignition energy in air	20 µJ
Autoignition temperature	1,085^{o}F (585^{o}C)
Volume expansion:	
Liquid (-252.9^{o}C) to gas (-252.9^{o}C)	1:53
Gas (from –252.9^{o}C to 20^{o}C)	1:16
Liquid (-252.9^{o}C) to gas (20^{o}C)	1:848

6.2 Primary Hazards

6.2.1 Burning

A hydrogen flame is nearly invisible unless it is colored by impurities. The temperature of burning hydrogen in air is high (3,718^{o}F), and warm hydrogen gas rises rapidly because of its great buoyancy. Hydrogen forms a flammable mixture with air at ambient conditions over a wide range of concentrations, 4 to 75 vol %.

The minimum ignition energy required for hydrogen (20 µJ) is about one-tenth the minimum ignition energy required for gasoline vapors. This minimum ignition energy can be provided when the static electricity accumulated by a person (10,000 to 20,000 µJ) is discharged. A high-pressure hydrogen leak will ignite from static electricity, from sparks from high-velocity rust particles, or other low-energy sources. Autoignition occurs at 1,085^{o}F.

6.2.2 Explosion

Once hydrogen is ignited, the reaction can proceed either by deflagration (subsonic propagation) or detonation (supersonic propagation). Deflagration in a closed volume can cause a pressure increase of almost 8 times the initial pressure. Detonation from a low-energy ignition source is possible in hydrogen-air mixtures of 18 to 60 vol % that are well mixed and confined. Although hydrogen-air mixtures have the same calorific value per pound as TNT (trinitrotoluene), the rate of energy release is much slower for hydrogen-air mixtures. Hydrogen detonations, although rare, are characterized by pressure increases so rapid that pressure relief devices are usually ineffective. When hydrogen is used in enclosed areas, NFPA Standard 69, “Explosion Prevention Systems,” should be consulted.

6.3 Safety Considerations

6.3.1 Assistance

Before installing a hydrogen system, prospective users of gaseous and/or liquid hydrogen should contact their ES&H representative and the C&LGSC for assistance in proper design and procedures. NFPA Standards 50A, "Gaseous Hydrogen Systems at Consumer Sites," and 50B, "Liquefied Hydrogen Systems at Consumer Sites," should also be consulted for design requirements. An HCP may be required for work with hydrogen. See LIR 300-00-01, "Safe Work Practices."

6.3.2 Liquid Storage Vessels

Liquid hydrogen is no longer routinely handled at the Laboratory. Special arrangements should be made though the CGPF to procure and receive liquid hydrogen. As with other cryogenic liquids, cryogenic hydrogen should only be used or handled by personnel who are familiar with its properties and skilled in the procedures necessary for its safe use. See LIR 402-580-01, "Cryogenic Fluids and Cryogens," for more information.

As stated in LIR 402-580-01, "Cryogenic Fluids and Cryogens," all liquid hydrogen storage Dewars must be electrically grounded and maintained at pressures greater than nominal atmospheric pressure to help insure that air does not diffuse in, freeze, and form a dangerous, potentially explosive, mixture. Because liquid hydrogen has a lower boiling point temperature, air condenses and freezes on surfaces that are at the temperature of liquid hydrogen. On an outside surface, frozen air will resemble white frost or snow. Oxygen separates from air as it liquefies. A shiny, shimmering surface may indicate the presence of liquid oxygen. Another indicator that liquid oxygen is present is its light blue color. This color may not be observable, depending on the quantity of liquid oxygen, available light, and colors of surrounding materials. Therefore, it is important to remember that the absence of the light blue color does not rule out the presence of liquid oxygen. However, the light blue color is a very good indicator of liquid oxygen presence when observed.

Liquid hydrogen's low heat of vaporization causes continuous boil-off even in a vacuum-insulated storage vessel (Dewar). However, the amount of gas given off during normal storage seldom creates a problem and can be handled by venting to a safe outdoor location.

Guidelines for vent systems are provided in CGA-5.5-1996, "Hydrogen Vent Systems," and NFPA 68, "Guide for Venting of Deflagrations." Vents on liquid hydrogen storage vessels should be designed to prevent air from condensing or diffusing back into the vents. A check valve near the top of a vent can prevent air backflow. Vents should be purged or evacuated both before and after use. Storage vessel lines containing hydrogen gas should be evacuated or purged with nitrogen or an inert gas before and after use. Storage vessel lines and volumes containing liquid or cold hydrogen should be evacuated or purged with helium before and after use because helium does not condense at liquid hydrogen temperatures. The effectiveness of the purge of vessels and systems should be verified.

6.3.3 Components

Piping and component materials that are not subject to hydrogen embrittlement or cold temperature embrittlement should be selected. Recommended materials include 300-series stainless steels, copper, aluminum, Monel, and some brasses and bronzes. Refer to LIR 402-1200-01, "Pressure, Vacuum, and Cryogenic Systems," for piping and pressure system design requirements.

As stated in LIR 402-1200-01, "Pressure, Vacuum, and Cryogenic Systems," pressure relief devices are necessary on all volumes where liquid hydrogen or cold hydrogen gas can be trapped and on vacuum insulation spaces surrounding liquid hydrogen.

After installation, all piping, tubing, and fittings should be tested and proved hydrogen-gas-tight at maximum operating pressure. All component volumes, including transfer lines, containing hydrogen should be evacuated or purged with nitrogen (at 77 K or above) or helium (below 77 K) before and after use. The effectiveness of the purge should be verified.

6.3.4 Storage and System Location

As stated in NFPA standards 50A and 50B, flame- and spark-producing devices and hot surfaces are prohibited in the vicinity of gaseous and liquid hydrogen systems. NFPA standards 50A and 50B should be followed for the safe storage and location of hydrogen and hydrogen systems.

6.3.5 Electrical Equipment

Any area where liquid or gaseous hydrogen is handled should be reviewed by knowledgeable people to determine the proper electrical classification (e.g., National Electric Code Article 500, "Hazardous Locations," Class I or II, Divisions 1 or 2, etc). Suitable electrical equipment (and proper installation) for hazardous locations may be necessary in addition to engineering controls, including the use of explosion-proof equipment (including ventilation fans).

6.3.6 Ventilation and Alarms

Because of its small molecular size, hydrogen can leak from small apertures through which other gases cannot pass. Ventilation with large quantities of air is vital to dilute small leaks of hydrogen to below the lower flammable limit of 4% in air. Whenever possible, hydrogen should be stored and used outside, with natural ventilation, or under a non-peaked shed roof, without walls. Indoor locations should have extensive ventilation adequate to handle the largest anticipated hydrogen leak or spill. Exhaust fans may need to be explosion-proof (see 6.3.5 above).

Wherever hydrogen is used indoors, flammable gas detection systems should be set to go off when the hydrogen concentration reaches 10% of the lower flammability limit. Sensors should be placed on or at the height of the ceiling immediately above the point of anticipated leakage. The alarm should be calibrated monthly, or in accordance with manufacturer's instructions, with a known hydrogen gas mixture.

While charging, storage batteries and battery banks evolve 0.016 ft^3 of hydrogen per ampere-hour per cell. Battery banks and storage batteries can thus be sources of hydrogen and should be located in adequately ventilated areas.

6.4 Emergency Response

If a person comes in contact with liquid or cold gaseous hydrogen, that person should be transported to the Occupational Medicine Group for medical treatment. If transportation for medical treatment is not immediately available, the affected area can be thawed with tepid water; however, the area should not be rubbed. The worker should then be transported to the Occupational Medicine Group for further treatment. Refer to Section 5.7 of LIR 402-580-01, "Cryogenic Fluids and Cryogens," for general cryogen emergencies.

When a gaseous hydrogen leak is discovered or when an alarm sounds, the following steps should be taken:

1. Evacuate the immediate area of all nonessential personnel.
2. Shut off the hydrogen source immediately (if possible) and vent all hydrogen to a safe outside location.
3. Eliminate any ignition sources in the area of the leak.
4. Increase indoor ventilation with emergency explosion-proof exhaust fans, if possible.
5. Implement emergency plan and make required emergency contacts.

To detect a *small*, local hydrogen fire (the flame is nearly invisible), use a small piece of tissue paper on a stick; the paper will readily ignite when it contacts a flame. If fire is present, the following steps should be taken:

1. Shut off the hydrogen source.
2. Let the fire burn itself out. (If the flame is snuffed out, it may reignite and cause greater damage.)
3. Use water spray to thermally protect people and equipment if the fire is hot enough to warrant it. A venting hydrogen flame cannot normally be extinguished with water.
4. Implement emergency plan (which should include calling the fire department) and make required emergency contacts.

Ultraviolet/infrared detectors and alarms should be installed on systems with the potential for large leaks.

7.0 Documentation

A hazard control plan may be required for operations involving hydrogen or hydrogen systems. Follow the requirements contained in LIR 300-00-02, “Documentation of Safe Work Practices.” Operating groups should also maintain design information for hydrogen systems and calibration records for hydrogen sensors.

8.0 References

8.1 Document Ownership

The office of institutional coordination responsible for this document is ESH-5.

8.2 Referrals

C&LGSC, 7-4240
Industrial Hygiene and Safety Group (ESH-5), 7-5231
Operational Safety Section of the Industrial Hygiene and Safety Group, 7-4644

8.3 Documents

Laboratory document LA-UR-98-2837, “Integrated Safety Management”

Laboratory document LIR 402-1200-01, “Pressure, Vacuum, and Cryogenic Systems”

Laboratory document LIR 402-580-01, “Cryogenic Fluids and Cryogens”

Laboratory document LIR 300-00-01, “Safe Work Practices”

Laboratory document LIR 300-00-02, “Documentation of Safe Work Practices”

Laboratory document LIR 402-510-01, “Chemical Management”

National Fire Protection Association, “Gaseous Hydrogen Systems at Consumer Sites,” NFPA Standard 50A (most recent edition)

National Fire Protection Association, “Explosion Prevention Systems,” NFPA Standard 69 (most recent edition)

National Fire Protection Association, “Liquefied Hydrogen Systems at Consumer Sites,” NFPA Standard 50B (most recent edition)

National Fire Protection Association, “National Electric Code,” Articles 500 and 501, NFPA 70 (most recent edition)

National Fire Protection Association, “Guide for Venting of Deflagrations,” NFPA 68 (most recent edition)

Compressed Gas Association, Inc. “Hydrogen,” Pamphlet CGA G-5, (most recent edition) www.cganet.com

Compressed Gas Association, Inc., “Hydrogen Vent Systems, “ Pamphlet CGA G-5.5-1996 www.cganet.com